TITLE: Development of Multi-Task Catalysts for the Removal of NO, and Toxic Organic Compounds during Coal Combustion

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ABSTRACT

OBJECTIVE

The goal of this project is to develop a catalyst for the oxidation of volatile organic compounds (VOC) and the reduction of NO in the presence of SOx and trace metals. Three primary objectives are described below:

1. Develop a fundamental understanding of the relationship between vanadium's valence state in the precursor solution and catalytic performance
   - Quantify the distribution of vanadium valence states in the precursor solution
   - Use XPS, Raman, FTIR, XRD, TPD, BET surface area and pore size distribution
   - Develop a method to quantitatively determine the amounts of anatase and rutile in polyoxide supports

2. Perform a parametric study on the best catalyst system
   - Observe the effects of different reaction conditions on catalytic performance
   - Vary reaction temperature, GHSV, and NO concentration

3. Study the best catalyst system under industrial conditions
   - Use a synthetic feed containing S02 and H20
   - Bum coal in a bench-scale combustor to provide a real feed stream

ACCOMPLISHMENTS TO DATE

A number of commercial titania supports have been used to study the effect of two different catalyst preparation methods. X-ray diffraction and nitrogen adsorption were used to examine the crystallographic structure, surface area, and pore size distribution of the supports. Supported vanadium pentoxide catalysts were synthesized by wet impregnation using either a newly made or aged vanadium oxalate solution. UVNIS spectroscopy and capillary electrophoresis were used to obtain the distribution of vanadium valence states in the precursor solution as a fimction of time, since our previous work (Economidis et al., 1999) determined that V+5 was reduced to V+4 over time. In addition, Degussa P25 titania was used to examine the surface interaction between vanadium pentoxide and titania at different degrees of thin layer coverage using selected combinations of vanadium valence states in the precursor solutions. YCPS, XRD, FTIR, and catalytic performance data were used to better understand the surface interactions between the thin layers of vanadium pentoxide and P25 titania. Samples of Ohio coals (Powhatan, Harrison, East Fairfield) have been received from FirstEnergy Corporation. The bench-scale combustor is currently being optimized to generate reproducible trials.

A number of trends were found in the catalytic data collected from the catalysts synthesized from commercial titania supports. First, high crystallinity titania (Aldrich) does not guarantee better catalytic activity when compared to other less crystalline forms of titania (Hombikat), which contradicts the earlier view supported by several research groups. Second, the rutile phase of titania (Kemira) is capable of providing substantial NO reduction under these conditions, when the anatase phase is usually preferred. Finally, catalysts prepared using a high surface area support (Hombikat) can perform just as well as other titania supports that contain other oxides (W03) that are used in industrial catalysts to enhance acidity. Other interesting results were found after comparing the activity data of catalysts synthesized using the newly made (V+5) or aged (V+4) vanadium oxalate solution. Our initial results showed that using V+4 during the wet impregnation process provided higher activity over a wider operating temperature range when compared to V+5; however, current results reveal a more complex trend that includes additional properties other than the valence state of vanadium in the precursor solution. Surface area appears to play a role in the performance difference of catalysts prepared by the two different wet impregnation methods. Low surface area supports show a greater difference in catalytic activity, while high surface area supports perform almost identically regardless of the vanadium precursor solution used. Our catalytic findings will be published in a series of papers. BET, FTIR, XRD, Raman, UVNIS, and XPS are currently being performed to help us understand the systems under investigation.

PLANS FOR THE COMING YEAR

- Correlate a fundamental understanding of vanadium's valence state in the precursor solution with observed surface phenomena
- Continue characterization with modem analytical techniques (XPS, XRD, Raman, FT-IR, TPD, UV-VIS)
- Investigate the parameter space for the most effective catalysts using a synthetic feed stream
- Study the most effective catalysts in the presence Of S02 and H20 using synthetic feeds and real feeds generated by burning selected high sulfur coals in a bench-scale coal combustor
- Proceed with kinetic studies to gain additional information about the surface of the catalysts

Articles, Presentations, and Students Receiving Support from the Grant Journal Articles (peer reviewed)

1) Economidis N. V., Pefia, D. A., and Smirniotis, P. G. "Comparison of Ti02-based Oxide Catalysts for the Selective Catalytic Reduction of NO: Effect of Aging the Vanadium Precursor Solution", *Applied Catalysis B: Environmental*, 23, 123-134, 1999.

2) Pefia, D. A., Jenkins, R. G., and Smirniotis, P. G. "DeNOx Catalysts with Controlled Valence of Vanadium for Optimum SCR Performance", in preparation for submission to *Journal of Catalysis* 2000.

3) Pefia, D. A., Jenkins, R. G., and Smirniotis, P. G. "Investigation of Ultrathin Vanadium Layers on Ti02 Support under Reductive and Oxidative Atmospheres", in preparation for submission to *Journal of Catalysis, 2000.*

4) Pefia, D. A., Jenkins, R. G., and Smirniotis, P. G. "Effect of Oxide Supports loaded with V4+ Species for SCR Reactions", in preparation for submission to *Applied Catalysis B: Environmental, 2000.*

Conference Presentations

1) Pefla. D. A., Jenkins, R. G., and Smirniotis, P. G. "Investigation of the Valence State of Vanadium during Impregnation for the SCR of NO using NI-13", presented at The Tri-State Catalysis Society Spring Symposium, Louisville, KY, April 20-21, 1999.

2) Pefia D. A., Jenkins, R. G., and Smirniotis, P. G. "The Role of V Valence State in the Precursor Solution of DeNOx Catalysts", to be presented at The l6th North American Meeting of the Catalysis Society, Boston, MA, May 3 O-June 3, 1999.

3) Peifta D. A., Jenkins, R. G., and Smirniotis, P. G. "Investigation of the Valence State of Vanadium during Impregnation for the SCR of NO using NI-13", to be presented at The 2000 Annual AlChE Meeting in Los Angeles, CA, November 12-17, 2000.

Students Receiving Support from the Grant.

Graduate Students:

1) Mr. Donovan Pefia, graduate (Ph.D.) student in Chemical Engineering
2) Mrs. Elizabeth Allen, graduate (M. S .) student in Chemical Engineering
3) Mr. Tianxin Zhang, graduate (M.S.) student in Chemical Engineering